2. That the temperatures at which the hissing just occurs, between 0° and 100° C., follow a law which may be expressed

$$V = C\,(\theta - t),$$

where V is the velocity of the stream at a temperature t, θ the critical temperature of water, and C a constant.

Experiments are being continued with other liquids, but the form of apparatus has to be modified with them, and we are not yet satisfied that the new form reproduces the required conditions.

Ionisation Potentials of Mercury, Cadmium, and Zinc, and the Single- and Many-lined Spectra of these Elements.

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[Plate 6.]

I. *Introduction.*

In a paper by Frank and Hertz in the 'Physikalische Zeitschrift,'* these investigators have shown that the minimum energy required to ionise an atom of mercury is that acquired by an electron in passing through a fall of potential of 4·9 volts. These writers have also shown in a later communication† that when heated mercury vapour is traversed by electrons possessing energy slightly above this amount the vapour is stimulated to the emission of the single spectral line $\lambda = 2536{\cdot}72$ Å.U. This result constitutes a new and most interesting application of the quantum theory, for it will be seen that in the relation $Ve = h\nu$, where $h = 6{\cdot}6 \times 10^{-27}$ erg sec., 4·9 volts is the potential fall which corresponds to the frequency ν of the line $\lambda = 2536{\cdot}72$ Å.U. If the relation just pointed out be applicable generally to all the elements it follows that if the vapour of an element can be shown to be capable of exhibiting a single-line spectrum, the frequency of this single spectral line may be used to deduce the minimum amount of energy required to ionise the atoms of that element.

With the object of establishing such a generalisation, if possible, some experiments were recently made by the writers, and it has been found that

* 'Verh. d. D. Phys. Ges.,' vol. 10, pp. 457–467.

† 'Verh. d. D. Phys. Ges.,' vol. 11, p. 512.

the vapours of cadmium and zinc as well as that of mercury can be stimulated to the emission of single-line spectra when traversed by electrons possessing the requisite amount of energy. With cadmium vapour the wave-length of the line constituting this single-line spectrum is $\lambda = 3260{\cdot}17$ Å.U., while that of the single-line spectrum of zinc vapour is $\lambda = 3075{\cdot}99$ Å.U. By the quantum theory it follows then that the minimum ionising potentials for cadmium and zinc vapours are respectively 3·74 volts and 3·96 volts.

II. *Apparatus.*

In carrying out the experiments the form of arc used is that shown in fig. 1.

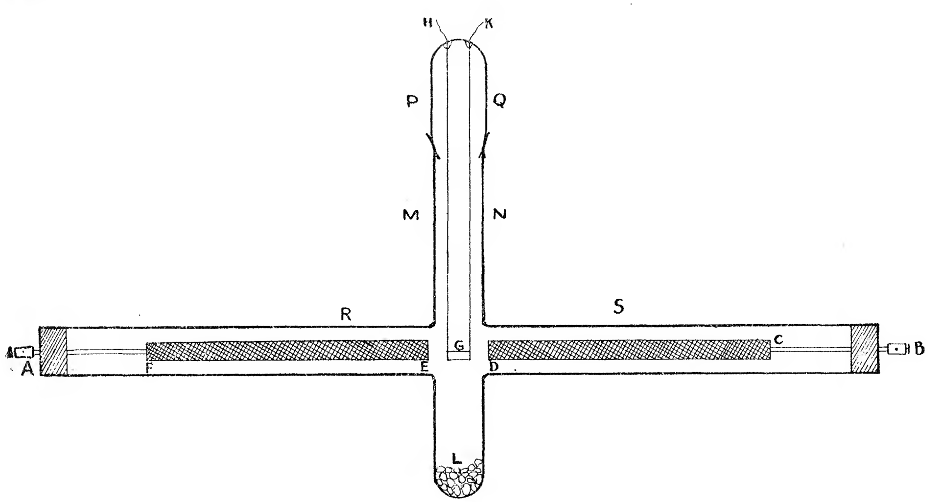


FIG. 1.

The apparatus consisted of a tube of fused quartz possessing three arms R, S, and MN, and a receptacle L. Some of the metal to be used in the arc was placed in the receptacle L, and two rods of the same metal FE and DC were attached to two wires and these latter were in turn fastened to two brass plugs, A and B, which were sealed into the tubes R and S with mastic wax. A small piece of sheet platinum was attached to two wires which constituted the heating circuit and these were sealed with platinum wire into a glass tube PQ at H and K. The open end of the glass tube PQ was ground so as to fit exactly into the end of the quartz tube MN as shown in the diagram. The arms MN, R, and S were each about 40 cm. long, and it was found with this length that when the receptacle L was strongly heated with a Bunsen burner the wax joints at A and B and the ground one at the end of the tube MN remained quite cool.

In the experiments the plate G was coated with a thin layer of either calcium oxide or barium oxide. When the tube was in operation the terminals of an auxiliary heating circuit were attached at H and K, B and K were joined by a wire and the arcing voltage was applied between B and A, the latter being the positive terminal. With this arrangement G and D constituted a double cathode. The tube was highly exhausted with a Gaede mercury pump through a glass tube which was sealed into an opening in the brass end-piece at A.

In taking photographs the plate G was brought to incandescence by means of the auxiliary heating current, the metal in L was strongly heated with the flame of a Bunsen burner so as to keep the plate G surrounded with the vapour of the metal, and the collimator of a small spectrograph with a quartz train was directed at the incandescent plate G. A short tube of asbestos was attached to the quartz tube directly in front of this plate, so that the radiation from the arc passed through it to the slit of the spectroscope. This arrangement was found necessary in order to cut off the radiation from the Bunsen flame itself. It should be noted that in studying the radiation from mercury vapour the electrodes CD and FE were simply stout iron wires.

III. *Characteristics of Arcs of the Different Metals.*

With the arrangement just described it was found that when the direct current 110-volt circuit, with suitable resistances in series, was applied to the terminals A and B, and the plate G brought to incandescence, strong arcs could be maintained for hours with all three metals. With the 220-volt circuit applied the arcs of all three metals could be made most intense, and could also be maintained for long periods. With the 220-volt circuit it was found that, when the arc was once struck, it could be easily maintained for a considerable time without the continued use of the oxy-cathode G. With low voltages, however, it was always necessary to maintain the plate G at incandescence in order to keep the arc established.

In commencing the investigation efforts were first directed to ascertaining the minimum voltages which should be applied between G and E in order to produce what may be called the many-lined spectrum of the different metals. These spectra are shown in the upper parts of figs. 2, 3, and 4. With mercury a difference of potential 12·5 volts was found to be necessary, with zinc 11·85 volts, and with cadmium 15·3 volts. With differences of potential below these respective values, but above 3 volts, it was found that the only spectrum which could be obtained for each of the metals was one which contained but a single line. Illustrations of these single-line spectra are shown in the lower portions of figs. 2, 3, and 4.

That for mercury, and shown in fig. 2, $\lambda = 2536{\cdot}72$, was obtained with an arcing potential difference of 9 volts, with an exposure of two hours and a-half. This single-line spectrum was also obtained with a potential fall of 5 volts, but it was only just visible on the plate with a five-hour exposure. With 3 volts and a five-hour exposure the line was not obtained. The continuous white band shown on the left of the spectrogram was due to the incandescent platinum. The line $\lambda = 3075{\cdot}99$ Å.U., shown in the lower spectrogram of fig. 3, was obtained with zinc vapour, with an arcing potential of 10·5 volts, with an exposure of three hours. According to the quantum theory relation, $Ve = h\nu$, this line should have been obtained with any potential difference above 3·96 volts, but no attempt was made with this element to ascertain with any exactness the least potential difference with which the line could be brought out.

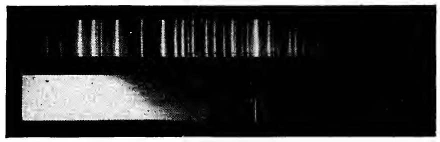
The line $\lambda = 3260{\cdot}17$ Å.U., shown in the lower spectrogram of fig. 4, was obtained with cadmium vapour, with an arcing potential difference of 13·6 volts. With an arcing potential of 3·4 volts and a three-hour exposure no trace of the line was obtained with this element. With this metal, as with zinc, no special effort was made to determine with any exactness the least potential difference which would bring out the line.

IV. *Discussion of Results.*

The investigation thus far has shown that it is possible to obtain spectra, each consisting of a single spectral line, with mercury, zinc, and cadmium vapours. To obtain these single-line spectra arcing potentials must be used which are lower than 12·5 volts, 11·85 volts, and 15·3 volts, which values have been found to be the minimum potential differences required to bring out the many-lined spectra for mercury, zinc, and cadmium respectively. From the work done with mercury, it would appear that the range of voltages which will bring out a single-line spectrum for an element is a very definite one, and extends from the potential difference corresponding to the frequency of the line given by the quantum theory to the potential difference which brings out the many-lined spectrum.

A point which should be mentioned in connection with this work is that, to bring out these single-line spectra, it was found that the best results could be obtained only when suitable vapour densities were used. The light corresponding to the lines in the single-line spectra of the three elements is known to be strongly absorbed by the respective vapours, and, if vapours of too great density be used, then the lines do not come out on the plates on account of absorption. On the other hand, if the vapours be too

FIG. 2.



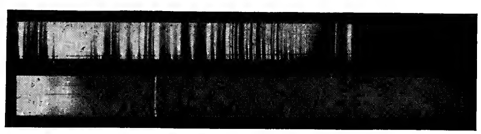
2536·72

FIG. 3.

3075·99

2139·3

FIG. 4.



3260·17

2288·79

rare, the intensity of the light is so weak that photographic traces of the lines cannot be obtained without extremely long exposures.

In attempting to offer an interpretation of the following facts: (1) that single-line spectra can be obtained with mercury, zinc, and cadmium vapours with a definite range of arcing voltages, (2) that the many-lined spectra for these elements are also obtainable with definite minimum arcing potential differences, and (3) that the conditions for obtaining these two classes of spectra are sharply differentiated, one cannot as yet speak with certainty. It will be recalled, however, that Sir J. J. Thomson,* in his work with positive rays, found that it was possible to ionise an atom of mercury in two, and only two, definite ways, that is, by removing either one electron from the atom or by removing eight of them. An obvious interpretation of his discovery would be that if an atom consists of a positive nucleus with one or more rings of electrons revolving about it, then the mercury atom may be supposed to have eight electrons in its outer ring, and that ionisation consists either in the removal of one electron from the atomic system or else in the removal of the whole eight electrons which constitute the outer ring. This may be taken to indicate that one can remove one electron, but only one, from the outer ring without completely destroying its stability. This explanation would fit in with the results described in the present paper, and it would seem, therefore, that the energy required to remove an electron from mercury, zinc, and cadmium atoms is that possessed by an electron which has passed through a fall of potential of 4·9 volts, 3·96 volts, and 3·74 volts respectively. To remove the outer ring of electrons from the atoms of these three elements the energy necessary would be that acquired by an electron under potential differences of 12·5 volts, 11·85 volts, and 15·3 volts respectively. The single-line spectra could then be explained by supposing that they had their origin in the recombination of the singly ejected electrons with the parent atoms, and on this view the explanation of the production of the many-lined spectra referred to above would be that they have their origin in the radiations emitted in the re-establishment of the complete outer ring of electrons in the atoms from which they had been removed.

In considering the probable range of wave-lengths covered by the many-lined spectra of the three elements, it may be pointed out that if the quantum theory be applicable the relation $Ve = h\nu$, combined with the minimum voltages which produce the spectra, enables one to calculate their upper limiting frequencies.

* Sir J. J. Thomson, 'Rays of Positive Electricity and their Application to Chemical Analysis,' p. 49.

With the values 12·5 volts, 11·85 volts, and 15·3 volts, it follows that the shortest wave-length in the many-lined spectrum of mercury should be given by $\lambda = 975{\cdot}3$ Å.U., while that in the spectrum of zinc should be given by $\lambda = 1281{\cdot}8$ Å.U., and that in the cadmium spectrum by $\lambda = 797$ Å.U.

It was pointed out by Paschen* in 1909 that the emission spectra of mercury, zinc, and cadmium should include a series of single lines represented by $\nu = 1{\cdot}5, \mathrm{S}-m, \mathrm{P}$. The limiting wave-lengths for these series are for mercury $\lambda = 1188$ Å.U., for zinc $\lambda = 1320$ Å.U., and for cadmium $\lambda = 1378{\cdot}7$ Å.U., which values it will be seen approximate to those calculated by the application of the quantum theory. The actual existence of the series lines represented by $\nu = 1{\cdot}5, \mathrm{S}-m, \mathrm{P}$, was demonstrated by Wolff† some two years ago, and members of the series were picked out by him as far down as $\lambda = 1402{\cdot}72$ Å.U. for mercury, $\lambda = 1376{\cdot}87$ Å.U. for zinc, and $\lambda = 1423{\cdot}23$ Å.U. for cadmium.

At present there appears to be no evidence of the existence of lines in the arc spectra of these three elements of wave-length shorter than those given by the relation $\nu = 1{\cdot}5, \mathrm{S}-m, \mathrm{P}$, so that it may very well be that the limiting lines of these series represent the limiting ones of the spectra arising from disturbances set up in the outer ring of electrons in the atoms of mercury, zinc, and cadmium.

The arcing voltages used by Wolff were higher than the lowest ones found by the writers in the present investigation to be capable of producing the many-lined spectra, but in all probability such higher voltages, while adding to the intensities of the lines obtained, would not add anything to the possible number of lines obtainable, unless these voltages were sufficiently great to produce disturbances in rings of electrons closer in to the nuclei of the atoms than the outermost ones. That disturbances in the inner rings of electrons are possible seems to be proven by the existence of Röntgen ray and γ-ray spectra. It would have been interesting to see if the series of lines $\nu = 1{\cdot}5, \mathrm{S}-m, \mathrm{P}$, predicted by Paschen and discovered by Wolff, were obtainable with voltages so low as those used in the present investigation, but, owing to the lack of a vacuum grating spectroscope, experiments to investigate this point could not be carried out by the writers.

It should be pointed out that the lines $\lambda = 2536{\cdot}72$ Å.U., $\lambda = 3075{\cdot}99$ Å.U. and $\lambda = 3260{\cdot}17$ Å.U. are respectively the first members of Paschen's‡ combination series $\nu = 2, p_2-m, \mathrm{S}$ for the elements mercury, zinc, and cadmium.

* Paschen, 'Ann. der Phys.,' vol. 30, p. 746 (1909), and vol. 35, p. 860 (1911).

† Wolff, 'Ann. der Phys.,' vol. 42, p. 825 (1913).

‡ Paschen, *loc. cit.*

V. *Summary of Results.*

1. It has been shown that a spectrum consisting of a single line is obtainable for mercury, for zinc, and for cadmium.

2. The wave-lengths of these lines are for mercury $\lambda = 2536{\cdot}72$ Å.U., for zinc $\lambda = 3075{\cdot}99$ Å.U., and for cadmium $\lambda = 3260{\cdot}17$ Å.U.

3. The minimum ionisation potentials for mercury, zinc, and cadmium have been shown to be 4·9 volts, 3·74 volts, and 3·96 volts respectively.

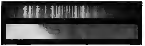
4. Some considerations have been presented which support Sir J. J. Thomson's theory of the two type ionisation of atoms of mercury, and others which suggest that the theory is applicable as well to the ionisation of atoms of zinc and cadmium.

5. The minimum arcing potential differences which will bring out the many-lined spectra of mercury, zinc, and cadmium vapours were found to be 12·5 volts, 11·8 volts, and 15·3 volts respectively. These voltages are also probably the minimum ionisation potentials of the second type for the atoms of these three elements.

6. Considerations have been presented which suggest the possibility of analysing the spectrum of an element in such a way as to enable one to correlate different portions of the spectrum with disturbances in definite portions of the atomic structure of that element.

The writers, in conclusion, wish to acknowledge their indebtedness to Mr. P. Blackman for assistance in taking the photographs and to Mr. F. Mezen for his help in blowing the quartz tubes.

Fig. 2.



2536·72

Fig. 3.

3075·99 2139·3

Fig. 4.

3260·17 2288·79